Polymer–Leather Composites. II. Kinetics of the Deposition of Selected Acrylate Monomers by Polymerization into Chrome-Tanned Cattlehide

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Synopsis

Limited kinetic information on a convenient process for depositing polymer in 5-oz cattlehide is presented in this article. The work includes a systematic study of the total polymerization rate and of the derived rates of deposition into the fibrous matrix, of bound polymer formation, and of polymer production in the external aqueous phase (the float) for three acrylic monomers. The monomers used, with a persulfate–bisulfite redox initiating system at 27°C, were methyl methacrylate (MMA), n-butyl acrylate (BA) and a fixed mixture of n-butyl acrylate and methyl methacrylate (BA + MMA). The effects of the reaction variables on rate, as measured by their intensity exponents, were not in agreement with a rate expression proposed to describe grafting in homogeneous polymerization, nor were they wholly compatible with classical and modified Smith–Ewart theories for heterogeneous emulsion polymerization. The experimental behavior, however, was in harmony with self-nucleation in the aqueous phase. Exponential orders of dependence were initiator > 0.5 (MMA, 0.72; BA + MMA, 0.66); monomer, zero; surfactant, ~0.5. The approximately 0.6 order dependence (MMA, 0.9) on leather amount was shown to be largely apparent and to decline as total polymerization proceeded. Thus a dominant grafting reaction was not supported. In support of this conclusion, simple impregnation of the matrix with preformed emulsion polymer yielded the same amount of bound polymer as that formed *in situ.* It was concluded that monomer is initiated largely from active centers formed initially near fibers or fibrils to form embryo polymer particles, which join penetrating swollen polymer particles and become unstable. These nucleate a polymer front, containing occluded radicals, which grows by diffusion regulated transport of monomer to complete deposition.

INTRODUCTION

The previous article[1] of this series[2,3] discussed briefly the rates at ambient temperature at which three acrylate monomers were deposited into or near the fibrous regions of leather. In that article a fixed set of reaction conditions was used with chrome-tanned 5-oz cattlehide in aqueous emulsion. These conditions had been shown[4–7] to be convenient and practical for preparing polymer–leather composites by persulfate–bisulfite redox initiation, with a wide variety of monomers.[8,9] The present article extends the previous work to include the effects of systematic changes in reaction variables on the kinetics of the reaction at ambient temperatures. It was expected that the kinetic information would provide insight into the mechanisms of the reactions involved and yield information concerning the role that grafting to collagenous substrates plays in guiding the overall polymerization reactions. Because data in the previous article[1] left considerable doubt that grafting was the dominant mechanism, this more intensive work seems especially relevant.

Most articles on the kinetics of chemically initiated polymerization of monomers in fibers have been limited to ceric ion redox systems of water-soluble or colloidal hydroxylated polymers[10-13] and appropriate model compounds.[14,15] Rates were proportional to the three-halves[16] or second order[15,16] in monomer concentration and one-half[13,16] or first order[15,16] in ceric ion and alcohol concentration. However, if the substrate was insoluble in water, graft yields fell dramatically.[17] Other proposed mechanisms for grafting to cellulose,[18,19] wool,[20] collagen,[21,22] and other natural fibers[23] usually required an assumption of primary radical attack on substrate to yield, through chain transfer, a graftable active center.[20,24,25] However, experimental support for this mechanism is infrequent.[20,22] Moreover, in the aqueous medium used, competing heterogeneous polymerization conditions prevail,[26-29] where radical capture by monomer swollen polymer particles often occurs in 1×10^{-5} sec.[27]

A major purpose of this article is to distinguish between the competing processes of primary radical grafting and emulsion polymerization to ascertain the dominant mechanism that controls polymer deposition and bound polymer formation in leather. This is accomplished here by observing the correspondence of the exponential intensity factors for the experimental reaction variables compared to theoretical values for the two mechanisms. To facilitate the stated purpose, overall rates of polymerization obtained in the present work were further separated experimentally into rates of deposition into the leather matrix, rates of bound polymer formation, and rates of polymerization in the float. Monomers used were, as before,[1] methyl methacrylate, MMA; n-butyl acrylate, BA; and a comonomer system of methyl methacrylate and n-butyl acrylate of fixed composition, BA + MMA, with 0.591 weight fraction of n-butyl acrylate. Conversions were usually limited to 40–50% to insure the measurement of interval II kinetics[29,30] (conversion range, 5–50%). The temperature was maintained at 27°C. Other information obtained includes rate data to 100% conversion, steady-state impregnation of monomer and preformed polymer, probable locus of initial monomer nucleation and monomer transport and its limitation in the composite growth process.

EXPERIMENTAL

Polymerization Conditions

Chrome-tanned 5-oz cattlehide strips (2.6 × 7.3 × 0.235 cm), including strips designated controls, were dried and equilibrated overnight with surfactant solution; the strips to be treated were polymerized with monomer by a similar procedure to that previously reported,[1] except that the 30-min pretreatment with the redox initiator was not used. Conditions designated standard in this work were as follows: monomer, 2.5 g; leather, 2.5 g (approximate weight of the above strips); Triton X100 (1.03%), 13.5 ml (five times dry leather weight plus one); potassium persulfate, 0.04 mole fraction based on the monomer; NaHSO$_3$/ K$_2$S$_2$O$_8$, 0.5; temperature 27°C; and time was varied. The composites and the float polymer (the polymer that formed in the aqueous phase) were isolated by previous procedures,[1] except the strips and float were short stopped with hydroquinone. Deposited polymer was then obtained gravimetrically and bound polymer estimated after benzene extraction.[1] These standard conditions, based

on a convenient practical method for preparing polymer–leather composite materials,[4-7] were used as points of departure in this work when changes were made in the experimental variables. Thus, the effect of varying the reactant concentrations on total polymerization rates were monitored by this procedure, as well as their effect on rates for both deposited and bound polymer formation within the matrix and for polymer produced in the float.

Other Procedures

Preformed BA + MMA polymer latex was prepared under standard conditions to 100% conversions (odor-free). Deposited and bound polymer present in the panels after impregnation with this latex were determined by the above procedures for six time increments to 5 hr; pickup rate was slow after 30 min. Monomer under standard conditions but with no activator present was permitted to permeate leather strips for six time periods up to 5 hr. Strips and latex were polymerized separately to 100% conversions in 24 hr by adding activator. The initial distribution of monomer between matrix and float was determined from a weight balance. Again little change occurred after 30 min. To determine the initial distribution of initiator between matrix and float, the leather strips, under standard conditions, were preconditioned for 30 min with surfactant solution containing the redox initiator. The strips and latex were polymerized separately for varied times by addition of monomer (both BA and BA + MMA, but no fresh initiator) and, for the strips, a new float. Composite compositions and latex polymer were determined. The distribution of initiator in the original partitioning was obtained from the relative reaction rates using the appropriate exponential intensity coefficient for initiator concentration to be given below. The effect of greater exposed surface on total rates and on rates of deposition and float polymer formation were obtained for panels ground in a Wiley* mill. The ground leather was treated by monitoring polymerization rate under standard conditions with BA + MMA monomer, but in one case with the float extended by 60% (concentrated system yielding a thick mush) and in another case with the float extended by 667% (dilute system). Comparisons were made by use of intact strips under the same conditions. Rough estimates of relative apparent diffusion constants were obtained by imbibition of lightly crosslinked BA + MMA sheet, 0.19 cm thick, with excess amounts of the three monomers in bulk at 27°C as a function of time until gravimetrically determined absorption became constant.[31] Repeat experiments gave similar values for the constants, and no polymer was removed by the procedure.

Definitions

In this work, mole fraction is designated m; weight fraction w; and monomer or other reaction variable molecular weights, MW. Subscripts are as follows: 1, leather; 2, polymer; d, deposited polymer; b, bound polymer; f, float; any other designations are defined in the text. Polymer composites are identified throughout by their monomer symbols: MMA, BA + MMA, and BA.

All experimental quantities were converted to quantities in mole/l. of water by use of eq. (1) for the concentration of the variable V.

* Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

$$[V] = [1,000(W/MW)]/\text{total water, cm}^3 \tag{1}$$
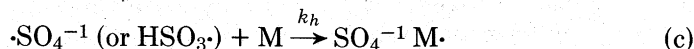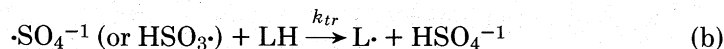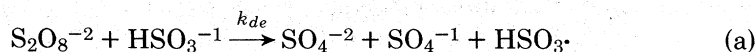
where W is weight in g. The pseudo-zero-order expression

$$[M]_0 - [M] = R_i t \tag{2}$$

where $[M]_0$ is the initial monomer concentration and $[M]$ the concentration remaining at time t, was used to estimate initial rates because the dominant rates of deposition in leather were constant with conversion often to 85%. Thus, rate, R_i, mol/l. sec, is the proportionality constant. Curve fitting was accomplished with an IBM 1130 computer.

THEORY

In the sections below, theoretical aspects of homogeneous grafting and heterogeneous polymerization kinetics are compared. These two processes are competing for initiating radicals under the experimental conditions usually used for polymer deposition in fibers.[4–7,20,24,25] Homogeneous grafting is treated first.

Most reactions leading to grafting are considered[25] to involve a primary radical attack on the substrate to produce active centers. For attack on collagen by persulfate–bisulfite initiation,[32] the pertinent reactions are the following:

$$S_2O_8{}^{-2} + HSO_3{}^{-1} \xrightarrow{k_{de}} SO_4{}^{-2} + SO_4{}^{-1} + HSO_3\cdot \tag{a}$$

$$\cdot SO_4{}^{-1} \text{ (or } HSO_3\cdot) + LH \xrightarrow{k_{tr}} L\cdot + HSO_4{}^{-1} \tag{b}$$

$$\cdot SO_4{}^{-1} \text{ (or } HSO_3\cdot) + M \xrightarrow{k_h} SO_4{}^{-1} M\cdot \tag{c}$$

$$L\cdot + M \xrightarrow{k_g} LM\cdot \tag{d}$$

$$M_n\cdot + M \xrightarrow{k_p} M_{(n+1)}\cdot \tag{e}$$

$$M_n\cdot + M_m\cdot \xrightarrow{k_t} M_{(n+m)} \tag{f}$$

where LH is leather, M is monomer, and where k values are specific rate constants for the reactions involved. The subscripts de, tr, h, g, p, and t for these and the kinetic expressions that follow are designated decomposition, transfer, homopolymer initiation, graft initiation, propagation, and termination, respectively. Here k_t represents the sum of the termination constants for termination by combination, k_{tc}, and disproportionation, k_{td}, respectively. Because in the overall reaction with [—HSO$_3$] fixed,[32] the initial rate of initiation of grafted chains, R_{ig}, is

$$R_{ig} = f'R_{tr} = f'k_{tr}[LH]2k_{de}[I] = f'k_{tr}[LH]R_{de} \tag{3}$$

where R_{de} is the rate of decomposition of initiator $S_2O_8{}^{-2}$, designated $[I]$, and R_{tr} the rate of transfer of tropocollagen protons to the primary radical. On the assumption that $k_h \sim k_g$, that is that eq. (d) reflects the same efficiency in starting

chain growth as eq. (c), then $f \sim f'$ where f_i are the usual efficiency constants. When the rate of grafting is large compared to homopolymerization, the rate of initiation will become dependent on the first power of the monomer concentration. Then, assuming biomolecular termination and, under steady-state conditions, the rate law becomes

$$R_p = k_p/(k_t)^{1/2}[M]^{3/2}[I]^{1/2}fk_{de}^{1/2} + (k_{tr}[LH])^{1/2} \qquad (4)$$

Thus, the overall rate of deposition when grafting is dominant is predicted to depend on the $3/2$ order of monomer concentration and to be $1/2$ order in both initiator and leather concentration. Here, leather concentration assumes soluble collagen; as shown below, the effective concentration becomes greatly reduced for out-of-phase collageneous fibers. In the absence of grafting, eq. (4) reduces to the normal rate law for homogeneous polymerization because [M] in the initiation step is eliminated.

$$R_d = k_p/(k_t)^{1/2}[M][S_2O_8^{-2}]^{1/2}(fk_d)^{1/2} \qquad (5)$$

For effective grafting, eq. (3) must exceed the rate of homopolymerizations R_{ih}; consequently, $k_{tr}[LH]$ must be large compared to k_h. This condition could be realized if reaction locus were exclusively in volume elements near fibril surfaces, brought about minimally by strong adsorption or complexation of initiator,[7,33,34] thus making [LH] large in local regions. The competing process of heterogeneous polymerization in highly divided states in aqueous medium is considered next.

The rate law for the nearly steady-state rate (interval II, conversion 5–50%) of polymerization in emulsion[26–29] is

$$R_p = -d[M]/dt = (k_p/N_A)(\rho_m/\rho_p)\phi_2 NQ \qquad (6)$$

where N_A is Avogadro's number; ρ, density of subscripts m (monomer), and p (polymer), respectively; ϕ_2 the volume fraction of monomer in the particle; N the number of particles; and Q the average number of radicals per particle [ideally 0.5 (ref. 26)]. Thus, in the ideal case, rate is proportional to only the number of particles and the monomer concentration per particle. The number of particles N depends on surfactant [S] and initiator concentration through[28]

$$N = 0.208 [S]^{0.6}R_i/K^{0.4} \qquad (7)$$

where $R_i = 2k_dN_A [I]$, and K is the volume growth rate of a particle. Equation (6) applies equally well to micellar stabilization and self-nucleation in aqueous dispersion.[35,36] If the colloid particles coalesce, the limiting Case III condition applies[26] and

$$R_p = k_p[M](V_pk_{de}N_A[I]/k_t)^{1/2} \qquad (8)$$

where V_p is the total volume of the polymer particles. This equation is identical in form to the normal rate law for homogeneous polymerization, eq. (5). When emulsion kinetics prevail, the exponential dependence is 0.4 in [I] and 0.6 in [S], but zero in monomer disappearance from the stabilized droplets in the aqueous phase.[26–29]

The above expressions provide a means of elucidating the pertinent mechanisms by comparing experimental with theoretical variable intensity exponents. The experimental environment just discussed favors heterogeneous polymer-

ization. Experimental data inserted into these expressions show that there are approximately 1×10^{14} particles per cm^3 and that radical capture therefore occurs in about 1×10^{-5} sec.[27] However, a better means of predicting the probability of grafting would be desirable. New developments in the basic science of heterogeneous polymerization make these predictions more feasible.

The concept of self-nucleation, proposed by Roe[37] and extended by Fitch et al.,[35,36] between dissolved monomer and initiator in the aqueous phase produces particles independent of the micelle concentration. As the soluble growing oligomeric radicals reach a critical size, dependent on their solubility and the temperature, they flocculate to form particles; these either capture other growing oligomeric radicals from solution and increase in size and stability or new particles are nucleated. Particle concentration becomes constant when the rate of radical capture becomes as large as particle nucleation at high particle concentration. After that, eq. (6) determines the steady state rate.

Thus, the foregoing discussion stresses that regardless of whether the initial particles are formed in micelles or by self-nucleation in the aqueous phase only oligomeric radicals would be available to approach fibrillar surfaces to initiate active grafting sites. Consequently, the probability of grafting can be estimated by use of expressions taken from the theory of Fox et al.[38] The ratio of the number of radicals terminating by radical–radical reactions to those terminating by chain transfer, at any conversion, α, is

$$y = y_0(1 - \alpha)C_s \qquad (9)$$

where the transfer constant C_s is defined as k_{tr}/k_p, and where the quantity y_0, which is amenable to experimental evaluation, is

$$y_0 = 2(k_t/k_p)^2(d\alpha/dt)_0/C_s[LH]_0 \qquad (10)$$

Initial grafting efficiency, ϵ_0, and efficiency at time t, ϵ, may then be computed.[38] Clearly if C_s is small in eq. (10) chain growth will be favored over chain transfer and ϵ_0 and ϵ can be shown to be small. Consequently, little grafting is predicted. Viscosity increase in the particles however, should increase ϵ_0 and ϵ somewhat because k_t in eq. (10) becomes smaller.

If the fibrous substrate is insoluble in the aqueous medium, [LH] reduces to [LH] effective, defined as

$$[LH]_{eff} = Af[LH]_0 \qquad (11)$$

where A is the fraction of tropocollagen chains at the surface of fibrils[1] and f is that fraction of amino acid residues that is labile. A calculation shows that A will be 0.0153 if f is taken as unity and the surfaces of fibrils are the loci of grafting. Thus, the requirement of only surface grafting to fibrils would greatly reduce its incidence per unit weight of collagen, although the grafting efficiency would remain unchanged in view of eq. (10).

RESULTS AND DISCUSSION

A. Estimates of Grafting Efficiency

Estimates of the parameters of eq. (10) and ϵ and ϵ_0 for several assumed values of C_s are presented for grafting to collagen by both methyl methacrylate and n-butyl acrylate in Table I. The value of C_s selected in experiments 1 and 4 is

TABLE I

Grafting Efficiencies Estimated by the Fox Relations for Assumed Values of Chain Transfer Constants

Experiment No.	System[a]	C_s[b] (assumed)	y_0	y ($\alpha = 0.5$)	F ($\alpha = 0.5$)	ϵ_0	ϵ ($\alpha = 0.5$)
1	MMA	1.8×10^{-4}	297	297	0.9998	0.00671	0.00354
2	MMA	0.66	0.0810	0.128	0.633	0.932	0.916
3	MMA	0.0534	1.0	1.04	0.964	0.625	0.623
4	BA	1.8×10^{-4}	17.2	17.2	0.9998	0.0581	0.104
5	BA	0.66	0.0047	0.0074	0.633	0.995	0.998
6	BA	3.10×10^{-3}	1.0	1.002	0.998	0.625	0.667

[a] Uses as $d\alpha/dt$ the constants k_d of Table V for standard conditions.

[b] C_s taken from ref. 41(c) for polymerizing MMA toward heptane, experiment 1 and 1-butenethiol, experiment 2; the same values were assumed for BA. In experiment 3 and 6, $R_b/R_h \sim 0.5$ so that $y_0 = 1.0$; C_s was calculated from eq. (10). Constants k_p and k_t are from ref. 41(d).

typical of residues containing many protons. In contrast, if C_s is large (~ 1.0) because residues are highly labile,[20] grafting probability will be large [neglecting eq. (11)]. With the assumption that the ratio of bound polymer rate to deposited rate is 0.5 (discussed below), as it often is in this work, the required C_s value and efficiency parameters were computed (experiments 3 and 6). A value of C_s as large as the tabled value for any tropocollagen residue[39,40] appears improbable.[41a] Thus, with certain reservations concerning the influence of declining k_t and the decrease of rates with conversion, these calculations provide little support for grafting as the dominant mechanism in creating bound polymer, especially in view of the further reduction per unit weight of collagen required by eq. (11). Actual experimental results are now compared with the predictions of theory.

B. Effects of the Reaction Variables

Table II lists rates of deposition, rates of bound polymer formation, rates in the external aqueous phase (float), and the total rate of polymerization for variation in both initiator concentration, [I], and leather amount, [L], for all of the systems studied. The rate of deposition R_d dominated the total rate, over a span of 40–50% conversion, for all systems. Because deposition conversion was linear with time (Figs. 1 and 2) at least over this time span,[1] diffusion control of deposition appears to be likely for all three systems. The linearity observed here is not merely a manifestation of interval II kinetics, because the upward curvature predicted by theory[29,30] was not observed. Bound polymer rates R_b (Table II) were generally about 0.4–0.5 of R_d, and R_b/R_d decreased with initiator concentration for the BA + MMA system. Thus, bound polymer rates were not a dependable constant fraction of R_d. Rates for BA + MMA in the absence of leather were similar to R_T for the system with leather, suggesting minimal dependence of rate on leather amount for this system. The total rate for MMA composites, however, appeared to be dependent on leather. More details are provided in the sections below on this and the other aspects of the kinetic data not shown in this table; the theory presented above is invoked to rationalize the results obtained.

Figure 1 shows typical data for the effect of initiator concentration, and Figure 2 shows the effect of leather amount for all experimental data comprising the

TABLE II

Initial Rates of Deposited, Bound Polymer and Float Polymer with Iniator and Leather Amount Varied for All Three Systems

Experiment No.	$[I]^a$ mole/l.	Rates (mole/l. sec), [I] variable[b]				$[L]^c$ mole/l.	Rates (mole/l. sec), [L] variable[d]			
		$R_d \times 10^5$	$R_b \times 10^5$	$R_f \times 10^5$	$R_t \times 10^5$		$R_d \times 10^5$	$R_b \times 10^5$	$R_f \times 10^5$	$R_T \times 10^5$
					Methyl methacrylate					
1	0.1945	27.5	11.7	1.20	28.7	1.96[e]	16.5	9.00	~0	16.5
2	0.1552	23.3	10.4	1.80	25.1	1.37	11.0	5.75	~0	11.0
3	0.0750	18.0	9.90	2.09	20.1	1.03	8.50	4.60	~0	8.50
4	0.0582	14.6	8.50	0.27	14.9	0.690	6.17	3.00	~0	6.17
5	0.0402	8.43	6.00	0	8.89	0.319	3.20	1.30	~0	3.20
6	0.0204	5.38	4.13	0	5.38	0	—	—	2.10	2.10
					n-Butyl acrylate-co-methyl methacrylate					
7	0.1687	8.50	4.50	10.7	19.15	1.96[e]	8.40	4.30	~0	8.40
8	0.1321	7.85	4.17	5.15	13.00	1.34	6.50	3.60	~0	6.50
9	0.0666	4.75	1.67	2.42	7.17	1.02	5.45	2.65	~0	5.45
10	0.0494	3.95	1.50	1.10	5.05	0.711	4.08	2.50	1.20	5.28
11	0.0333	2.97	1.33	0.725	3.70	0.341	2.75	1.15	2.00	4.75
12	0.0157	1.87	0.440	0	2.39	0	—	—	8.25	8.25

			n-Butyl acrylate			
13			1.98[e]	5.00	~0	
14			1.26	4.00	~0	
15			0.960	3.00	~0	
16			0.625	2.40	~0	
17			0.302	1.45	~0	
18			0	14.00	~0	14.0
		N-Butyl acrylate-co-methyl methacrylate, no leather				
19	0.1687		14.50	14.50		
20	0.1321		12.50	12.50		
21[e]	0.0666		9.75	9.75		
22	0.0494		7.75	7.75		
23	0.0323		6.43	6.43		
24	0.0164		4.53	4.53		

[a] All concentrations based on mole/l. of water.

[b] Fixed concentrations were in mole/l. MMA—[M], 1.954; [L], 1.957; [S], 0.0163; BA + MMA—[M], 1.693; [L], 1.960; [S], 0.051; BA + MMA, no leather—[M], 1.693; [S], 0.0163.

[c] Leather and monomer concentrations, although insoluble, also based on water.

[d] Fixed concentrations were in mole/l. MMA—[M], 1.863; [I], 0.0742; [S], 0.0163; BA + MA—[M], 1.609; [I], 0.0631; [S], 0.0163; BA—[M], 1.460; [I], 0.0585; [S], 0.0163.

[e] These experiments were prepared under approximately standard conditions. They are set in final form in Table V.
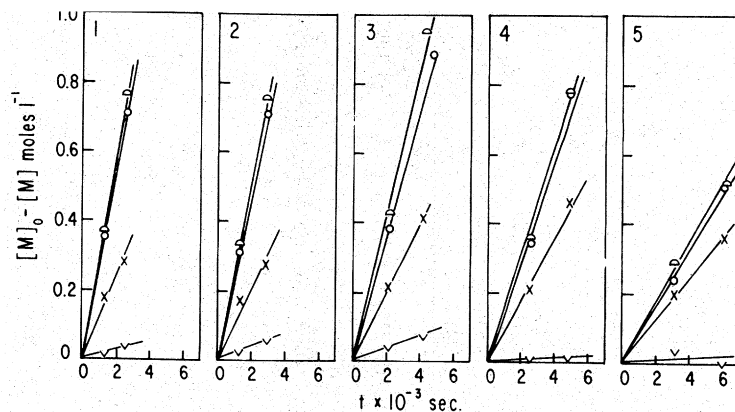
Fig. 1. Rate of monomer consumption vs. time for the MMA composite systems of Table II at varied initiator concentrations. Inserts correspond to their experimental numbers in the table (experiment 6 not shown). The order of the rate curves in each insert, top to bottom, is R_T ($\triangle$); R_d (O); R_b (X); R_f (v).

total polymerization rates with MMA. A conversion span of about 50% is covered for the standard condition experiment (insert 3, Fig. 1, and insert 1, Fig. 2). Thus the conversion span of interval II was largely encompassed as illustrated in the figures.[29] The paucity of data points reflected the laboriousness of the gravimetric procedure used to obtain the rate data; the scatter resulted from the marked variability of leather composition, even for adjacent samples, as demonstrated in a previous article.[1] The order of the initial rates was $R_d > R_b > R_f$ in both figures, as well as for most of the initial rate data in this article. Noteworthy is the exponential increase in float rate in Figure 2, which generally increased as leather amount decreased. The significance of this is demonstrated below.

Plots of $\ln R_d$ and $\ln R_b$ vs. $\ln$ [I] shown in Figure 3 follow the general expression

$$R_i = R_{i0}[V]^a \tag{12}$$

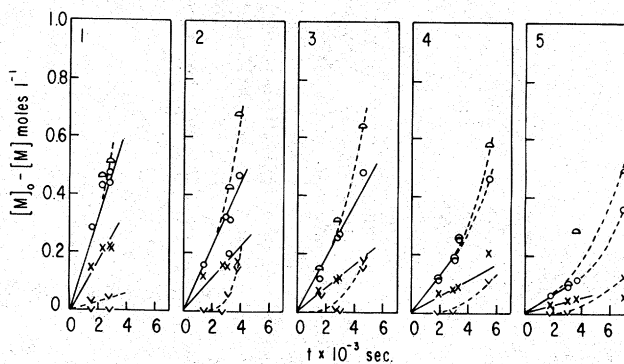R_i is any rate, V the reaction variable, and R_{i0} and a are constants. Values of

Fig. 2. Rate of monomer consumption vs. time for the MMA composites of Table II at varied leather amounts. Inserts correspond to their experimental numbers in the table. The order of the rate curves in each insert, top to bottom, is R_T (- - -) ($\triangle$); R_d (—) (O); R_b (—) (X); R_f (- - -) (v).
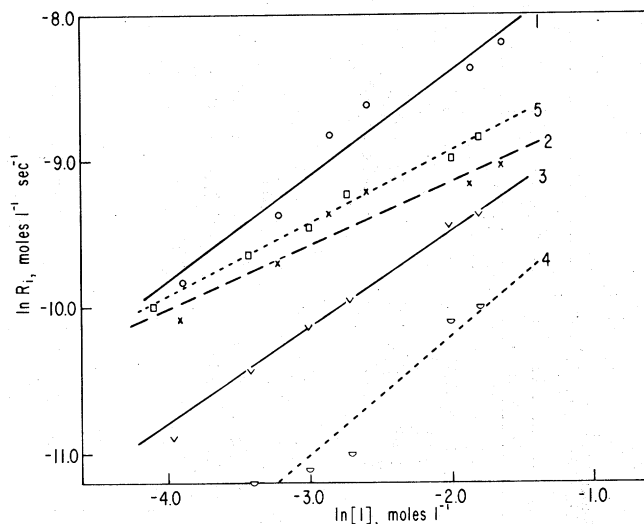
Fig. 3. Rate of R_i vs. the initiator concentration [I], plotted in accordance with eq. (12) for the following systems: curve 1, MMA R_d, curve 2, MMA R_b; curve 3, BA + MMA R_d; curve 4, BA + MMA R_b; curve 5, BA + MMA, no leather.

R_{i0} and the intensity constant a for the variables used with all of the systems are given in Table III. In the figure and in the table under initiator concentration, [I], the exponents a for R_d for both the MMA and BA + MMA systems are similar, but for R_b they are different. More scatter accompanied this and the other R_b-variable plots. Because of this scatter and especially because of the large change in exponents a for monomers of similar reactivity, R_b appears to be a trivial result of the formation of deposited polymer. Of equal importance is that the magnitude of a in the absence of leather was less than that for composite formation; the significance of this is also discussed below.

All data for monomer depletion with time fell on common curves for R_d, R_b, and R_f, as is shown in Figure 4 for MMA composites and in Figure 5 for those with BA + MMA. Thus, rates were independent of monomer concentration (Table III). This is the expected result [eq. (6)] for heterogenous polymerization at a colloidal state of subdivision where rate is dependent on the equilibrium monomer concentration of the particles, as in set 10; even a slight perturbation of the R_d curves[29] produced when $Q > 0.5$ [eq. (6)] can be observed in both figures. However, polymerization in aggregates, when rates are regulated by diffusion of monomer to active sites, would produce similar results. Dependence of the log of rate on the state of subdivision is also reflected in the rate dependence on the logarithm of surfactant concentration [Table III, Fig. 6, and eq. (7)]. Data to the right of a critical surfactant concentration (0.0301M/l. for MMA composites, insert A, and 0.0143M/l. for those using BA + MMA, insert B) fall on a straight line, yielding the exponent a of eq. (7), while those on the left show anomalously increased rates. Because considerable flocculation was noticed in the low surfactant experiments (those to the left in both inserts in the figure), the effect illustrated was attributed to instability resulting from partial desorption of the protective colloid from the particles to the leather matrix. Gel effect would then produce the increased rates. The discontinuity was not seen in the absence of leather (dotted line in insert B).

TABLE III

Exponential Intensity Constants for the Reaction Variables of All Composite Systems

| Set No.	Reaction variable	R_d (mol/l. sec)		R_b (mol/l. sec)	
		$R_{i0} \times 10^5$	a	$R_{i0} \times 10^5$	a
		Methyl methacrylate systems			
1	[I]	97.0 ± 3.19	0.723 ± 0.082	26.0 ± 0.673	0.444 ± 0.077
2	[M]	18.2	0	9.15	0
3	[L]	8.61 ± 0.0021	0.885 ± 0.032	4.36 ± 0.0076	1.05 ± 0.028
4	[S]	55.8 ± 0.229	0.509 ± 0.011	15.5 ± 0.226	0.294 ± 0.040
		n-Butyl acrylate-co-methyl methacrylate systems			
5	[I]	45.7 ± 0.243	0.657 ± 0.016	20.0 ± 0.764	0.841 ± 0.123
6	[M]	7.30	0	4.25	0
7	[L]	5.29 ± 0.033	0.636 ± 0.106	2.78 ± 0.0139	0.745 ± 0.072
8	[S]	48.3 ± 0.608	0.494 ± 0.207	20.9 ± 0.289	0.480 ± 0.033
9	[I] no leather	35.8 ± 0.280	0.500 ± 0.021		
10	[M] no leather	8.23	0		
11	[S] no leather	207.0 ± 7.72	0.793 ± 0.054		
		n-Butyl acrylate systems			
12	[L]	3.23 ± 0.007	0.667 ± 0.032	3.30 ± 0.0020	0.702 ± 0.032
13	[M]	5.60	0		
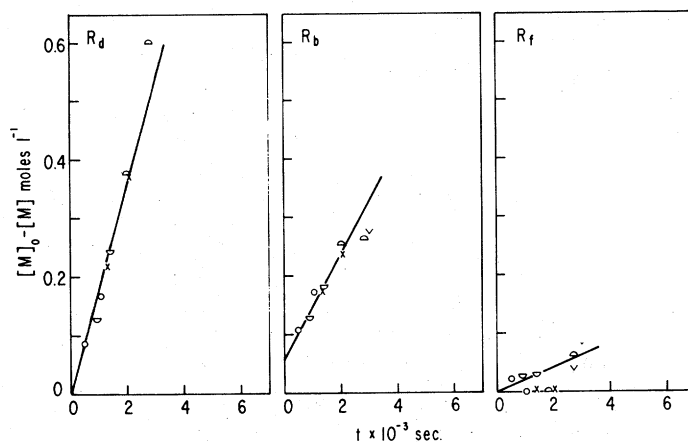
Fig. 4. Rate of monomer consumption vs. time for the MMA composites with monomer concentrations varied. MMA concentrations used were O, 0.487 mole/l.; ☋, 0.816 mole/l.; ✕, 1.28 mole/l.; △, 1.92 mole/l.; v, 4.85 mole/l.; all based on water.

The significance of the exponential intensity dependence of the variables in Table III on the rates of deposition are now considered. Values of a for initiator in both MMA and BA + MMA composite formation are considerably greater than the 0.4 dependence specified by eqs. (6) and (7) for heterogeneous polymerization and by eqs. (4) and (5) for homogeneous polymerization, except for BA + MMA polymerization in the absence of leather. While values of $a = 0.5$ are found for stable latices in the polymerization of vinyl acetate[42] and vinyl chloride,[43] these monomers have considerable water solubility and terminate by chain transfer. Consequently they probably constitute special cases. The pattern of results in the table and the observed buildup of polymer in the leather[1] suggest that particle aggregation caused the reaction kinetics to pass from those characteristic of heterogeneous to that found for homogeneous systems, thus producing Case III conditions [eq. (8)]. Values of $a > 0.5$ for initiator dependence
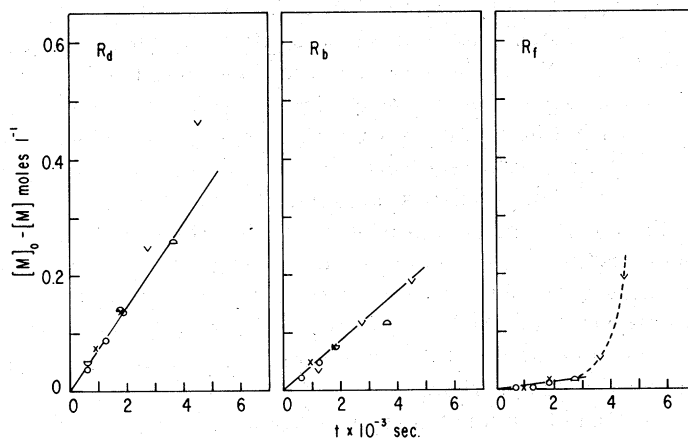

Fig. 5. Rate of monomer consumption vs. time for the BA + MMA composites with monomer concentrations varied. The BA + MMA concentrations used were O, 0.432 mole/l.; ☋, 0.746 mole/l.; ✕, 1.096 mole/l.; △, 1.70 mole/l.; v, 3.34 mole/l.; all based on water.
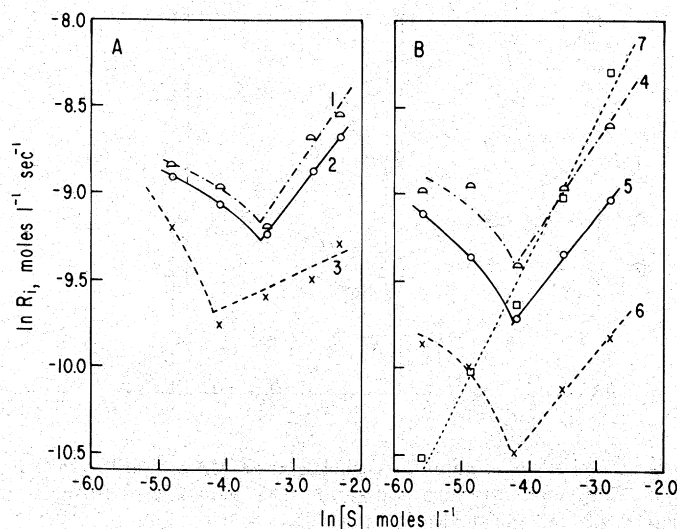
Fig. 6. Rate R_i vs. the surfactant concentration [S] plotted in accordance with eq. (12) for insert A, MMA composites, and insert B, BA + MMA composites. Curve 1, R_T; curve 2, R_d; curve 3, R_b; curve 4, R_T; curve 5, R_d; curve 6, R_b; curve 7, no leather. The discontinuity in curves 1–6 represents the region of assumed protective colloid instability.[1]

could only result from delayed termination through radical scavenging. A strong gel effect was also shown from molecular weight data in the previous article[1] and is typical of polymers depositing in fibers.[18-25] Qualitatively, the effects of monomer and surfactant concentration support heterogeneous polymerization, but subject to the diffusive alternative with respect to monomer concentration discussed above. However, the predicted dependence of 0.6 on surfactant concentration [eq. (7)] was not found, even in the absence of leather.

The apparent strong dependence of rate on leather amount (Tables II and III) is deceiving. The data in the tables consider only initial rates for polymerization in the float. When the time period was extended to 1 hr (Table IV), where total monomer conversion was around 20–25%, rates in the float started to equal those for deposition in the fibers (BA + MMA) or greatly exceeded (BA system) the deposition rates as leather amount was incrementally reduced. By this time, the total rate for BA + MMA was nearly the same as in the absence of leather and thus no longer depended on leather amount (Fig. 7). The total rates with no leather and with diminishing leather amount approached each other in the BA system. Only in MMA composites did the leather concentration appear to have a long time influence on deposition rate. The rate enhancement here could reflect a decreased k_t in the viscous medium. Thus the rate would increase with leather amount as the confined polymer volume increased. It may be concluded that leather amount strongly influenced the nucleation period of aggregate development in the leather fibers.[1] However in the steady-state period of deposition, rates between float and matrix became more competitive and were accompanied by a strong gel effect.

The dependence of bound polymer formation on the reaction variable through eq. (12) was very erratic and the individual data were somewhat scattered compared to those for deposited polymer (Figs. 3 and 7, and Table III). Bound polymer formation appeared to be a secondary consequence of polymer depos-

TABLE IV

Effect of Leather Amount on the Rates of Polymerization in mole/l. sec in the Float at 3600 sec

Experiment No.	[L] (mole/l.)	$R_d \times 10^5$	$R_b \times 10^5$	$R_f \times 10^5$	$R_t \times 10^5$	% Conversion
			Methyl methacrylate			
1	1.964	16.5	9.00	1.67	18.2	30.5
2	1.374	11.0	5.75	2.64	13.6	21.0
3	1.027	8.50	4.60	1.94	10.4	25.0
4	0.6895	6.17	3.00	0.778	6.95	14.0
5	0.3187	3.20	1.30	0.417	3.62	9.0
6	0	—	—	2.10	2.10	4.2
			n-Butyl acrylate-co-methyl methacrylate			
7	1.963	8.40	4.30	0.556	8.96	20.0
8	1.338	6.50	3.60	1.11	7.61	23.6
9	1.020	5.45	2.65	3.33	8.78	17.8
10	0.711	4.08	2.50	4.86	8.94	17.0
11	0.341	2.75	1.15	5.56	8.31	18.2
12	0	—	–	9.75	9.75	18.6
			n-Butyl acrylate			
13	1.975	5.00	—	0.556	5.56	17.0
14	1.259	4.00	—	1.67	5.67	13.5
15	0.960	3.00	—	2.08	5.08	6.0
16	0.625	2.40	–	4.86	7.26	19.0
17	0.302	1.45	—	25.0	26.5	90.8
18	0	—	—	27.8	27.8	100.0

iting in fibers. The behavior seemed, therefore, to indicate incomplete removal of homopolymer or chaotic adventitious crosslinking and thus to reflect the variable tenacity of different leathers in causing homopolymer entrapment during solvent extraction.[1] These observations do not support dominant grafting; if a grafting reaction guided deposition, a more consistant pattern would be observed in the results in Table III for the different systems, and a closer correlation with theory through eq. (4) should have been found.
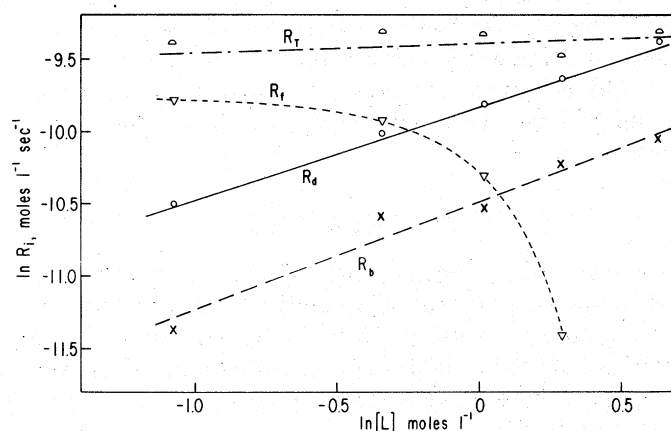

Fig. 7. Rate R_i vs. the leather amount [L] for the BA + MMA composites at 3600 sec, plotted in accordance with eq. (12).

C. Proposed Deposition Mechanism

Acrylic monomer deposition in cattlehide leather fibers appears to be a heterogeneous process, initially, that assumes the character of a homogeneous process as polymer flocculates and grows as a bulk phase in the system. Thus a progression from largely interval II, Case II kinetics eq. (6) to essentially Case III[26] kinetics [eq. (8)] seems to occur but with some intensity exponents perturbed by the gel effect. In this mechanism the persulfate redox ions distribute themselves in equilibrium concentrations in the internal stationary aqueous phase around fibers and encompassing fiber bundles, by preferential adsorption at fast rates,[7] and perhaps they are even adsorbed at specific sites on fibrils. For example, $\cdot SO_4$ might be ionically attracted to the cationic protein and Cr complex. Growing polymer particles, formed by self-nucleation in the external water phase or in micelles penetrate the fine collageneous structure and become unstable. These join larger monomer swollen particle populations already formed in the matrix as a result of the persulfate concentration gradient. These two colonies of flocculating particles, one formed *in situ* and the other invading from the external float, would tend to concentrate the initial aggregates in those fibers located near leather surfaces. The aggregates would tend to nucleate the layered growth pattern, such as the sandwich effect in cattlehide discussed at length in the previous article.[1] Whether the specific deposition locus is in the fine structure near fibrils, thus expanding fibers on propagation, or more coarsely deposited around fibers, thus expanding fiber bundles with continued deposition, is not clear because both growth mechanisms would produce similar effects on density–composition curves.[1] Following nucleation, the aggregate propagation period commences, fed by slow diffusion of monomer from the colloidal droplets, through the growing polymer front, to the occluded active centers. This growth expands the fibers or fiber bundles and produces the changes in density discussed in detail in the previous article. When the growth front reaches the surface, polymerization activity accompanied by enhanced rates from the increase in active centers is transferred largely to the float. Matrix deposition then slows,[1] becoming only a surface growth that embeds fibers. As discussed above, considerable bound polymer could result from the intimacy of its deposition in inaccessible regions of the fine structure. Much of that which was grafted either to collagen or by prolific polymer–polymer branching to form networks would be produced in compliance with the magnitude of the parameters of eq. (10). Primary radical grafting would account for the balance.

Data are introduced in the sections below that will lend additional support to these concepts as well as provide new insights into the mechanism of this complex process.

D. Overall Yields

Table V and Figure 8 present the rates of deposition and of bound polymer formation under the standard reaction conditions outlined in the experimental section and in the previous article,[1] when polymerization was carried to 100% conversion with all of the available experimental data. These rates are similar to those in Table II, where conversions were limited. Some of the leathers were conditioned 30 min in the redox reagents, but most were not; the random distribution of data points indicated that this treatment was not necessary. The

Set No.	Monomer	Reactant concentrations, mole/l.				$R_i \times 10^5$ (mole/l. sec)		$k_i \times 10^5$ (sec^{-1})
		$[I]^{a,b}$	$[M]^b$	$[L]^b$	$[S]^b$	R_i	error	
1	MMA, dep.	0.0746	1.885	1.967	0.0163	16.61	±0.56	8.81
2	MMA, bound	0.0746	1.885	1.967	0.0163	8.08	±0.31	4.29
3	BA + MMA, dep.	0.0660	1.674	1.967	0.0163	7.67	±0.27	4.58
4	BA + MMA, bound	0.0660	1.674	1.967	0.0163	4.27	±0.13	2.55
5	BA, dep.	0.0600	1.509	1.967	0.0163	5.38	±0.28	3.56
6	BA, bound	0.0600	1.509	1.967	0.0163	2.47	±0.097	1.64

[a] $[I]/[M] \sim 0.04$.

[b] All concentrations and rate data based on water amount.

appreciable scatter (Fig. 8) again reflects leather density variability when used to monitor rates by a gravimetric procedure.[1] The data were significantly linear by computer fit and not concave upward, as predicted for interval II kinetics,[29] and thus add to the evidence provided above that flocculant growth, rather than the state of subdivision, controlled rates through much of the deposition. Because rates were independent of monomer concentration in the aqueous phase, the quantities k_d and k_b are system constants with first-order dimensions that also represent the fractional extent of conversion $d\alpha/dt$ (Table I).

E. Additional Supportive Data

The data in Table VI provide additional support to the mechanism of deposition first discussed. All of the data were obtained by procedures outlined in the second portion of the Experimental section. The ratio $[I]/[I]_0$ is the fractional distribution of persulfate ion in the matrix after a 30-min pretreatment. The statistical equilibrium ratio is 0.28. The values for the two systems in the table agree with a value of 0.778 in 30 min calculated from the titrometric data of Harris et al.[7] Thus, preferential migration of initiator within the fiber region, postulated previously[7] and in section C, is supported. Rates of adsorption of persulfate ion apparently exceeded deposition rates (Table V, section D) because the pretreatment had no apparent effect on the magnitude of k_d and k_b. However, the hydrated matrix tended to exclude monomer because the ratio $[M_d]/[M_T]$, column 8, was even less than the statistical ratio 0.28, even after 5 hr. Because growing particles in emulsion systems usually contain 75–80% monomer,[45] the collageneous material was relatively deficient in monomer. This lends support to the primacy of the floculating emulsion process proposed in sections B and C. It is especially significant that mere impregnation of hydrated leather with preformed BA + MMA latex yielded about half the amount of unextractable polymer $[P_b]$ (column 5) as that deposited (column 4). These quantities represent an average of six separate experiments with time of impregnation varied. Thus, the presence of active centers are apparently not required to produce
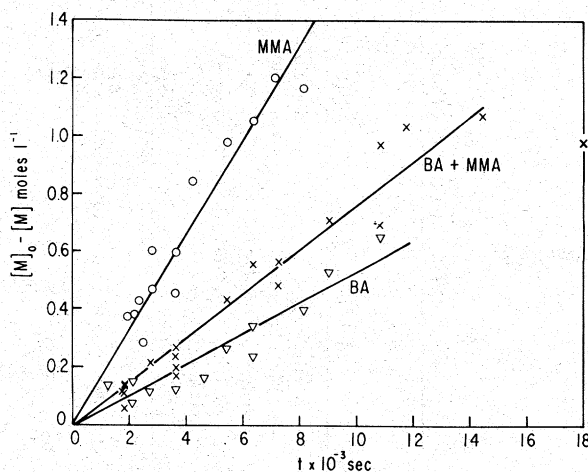

Fig. 8. Rate of polymer deposition in leather vs. time to 100% conversion for all three systems at standard conditions (Table V) with all of the available data combined.

TABLE VI
Steady–State Rate Constants, Initiator Distributions, Monomer and Polymer Impregnation Results, and Effect of Ground Leather on Polymerization Rate

System	$k_d \times 10^5$ (sec^{-1})	$[I]/[I]_0$[a] (after 30 min)	Leather impregnation, preformed polymer			Leather impregnation monomer		Deposition in ground leather		
			$[P_d]$[b] (mole/l.)	$[P_b]$ (mole/l.)	$[P_d]/[P_T]$	$[M_d]$[c] (mol/l.)	$[M_d]/[M_T]$	$k_d \times 10^5$ (sec^{-1})	$k_f \times 10^5$ (sec^{-1})	$k_T \times 10^5$ (sec^{-1})
MMA	8.81	0.692								
BA + MMA	4.58	0.740	0.193	0.103	0.118	0.103	0.0644			
BA	3.56									
Powd., conc.[d]								22.1	6.18	28.0
Intact, conc.[d]								4.53	4.72	8.02
Powd., dil.[d]								4.15	32.5	40.4
Intact, dil.[d]								1.45	9.69	11.8

[a] [I] is the initiator concentration in the leather; the statistical ratio is 0.277.

[b] Initial polymer concentration in the emulsion was 1.638M/l. $[P_d]$ and $[P]_b$ represent the average polymer concentration found for six impregnation experiments, of varied times between 0.5 and 5 hr.

[c] Initial monomer concentration in the emulsion was 1.638 mole/l.

[d] BA + MMA monomer. In the concentrated systems, monomer concentration was 1.13 mole/l.; dilute systems, 0.277 mole/l.; standard conditions, 1.67 mole/l.

unextractable polymer, as implied in section C. When more collageneous surface was exposed by grinding the leathers (last three columns) a large increase in the deposition rate constant, k_d, was observed for polymer depositing in a thick paste of swollen fiber compared to the corresponding intact leather. On dilution with more water, however, the constants for total rates, k_T, and for rates in the float, k_f, were now abnormally large compared to k_d. A controlling grafting mechanism, operating in a dispersion of short fibers would be expected to produce large k_d because of greater surface exposure and small k_f because of enhanced grafting efficiency [eq. (11)]. Reasons for the strong Tromsdorff rate accelerations noted for the ground systems and the small value found of k_d found for the dilute intact leather system compared to the correct value (column 2) are not understood at present.

Finally, the influence of the monomer used on diffusion through the polymer layer on the relative rates of deposition for the three acrylate monomers used remains to be treated. Insert A, Figure 9 shows good correlation of a plot of the system deposition efficiency constants D_e (equal to w_2/w_2 feed) (ref. 1) for the three monomers plotted (solid line) as a function of the reciprocal of the deposition rate constant k_d (Table V). A similar plot (dashed line) of rate data given in the previous article[1] is shown after conversion to k_d using R_d [M]. Thus, the system efficiency was directly proportional to the rate of deposition regardless of float volume. These rate constants, k_d are also directly proportional (insert B) to the apparent diffusion constants for the three monomers imbibed into a thick BA + MMA film. The magnitude of the constants specify rapid diffusion through the polymer phase. This is not at variance with known diffusion rates[45] for like monomer–polymer pairs having, as in this work, similar solubility parameters for monomers and polymers.[41b] Although the D_a values observed are accurate only as relative values, the close correlation observed with k_d provides encouraging evidence for diffusive transport of monomer to expand the polymer phase as proposed in section C.
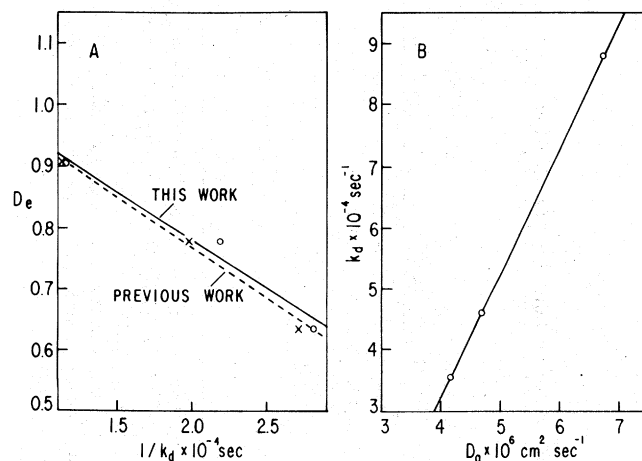

Fig. 9. Relation (insert A) between the system efficiency constant D_e of the previous article[1] and $1/k_d$ of this work (from Table V), and that calculated from the data in Table III of the previous work. Insert B illustrates the relation between k_d of this work and the apparent diffusion constant D_a for the monomers through BA + MMA panel. Values of $D_a \times 10^6$ cm²/sec were MMA, 6.72; BA + MMA, 4.69; and BA, 4.16.

SUMMARY AND CONCLUSIONS

This work ascertained the effects of systematic changes in the reaction variables on rates of deposition, bound polymer formation, polymerization in the float, and total polymerization for the emulsion polymerization of three acrylate monomer systems at 27°C in the presence of 5-oz cattlehide. A potassium persulfate-sodium bisulfite redox system was used as the initiator. The results showed no direct correlation with any single theory derived either to explain grafting through homogeneous polymerizations or to characterize heterogeneous polymerization in a subdivided state. Instead, exponential intensity coefficients for the reaction variables indicate a transfer of mechanism from heterogeneous to homogeneous polymerization as monomer swollen polymer particles are flocculated after penetration of the aqueous leather matrix near fibers or, perhaps, fibrils. These become the favored loci because of fast migration of persulfate ion to this region. Aggregating polymer particles containing occluded radicals thereafter constitute a growth front that expands in fibers or fiber bundles located near specimen edges. Thus, the growth front is maintained at a constant expansion rate by slow diffusion of monomer to active centers.

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